COATINGS. ENAMELS

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ALKALINE TITANIUM-SILICATE GLASSES FOR WHITE GLASS ENAMELS WITH ENHANCED CORROSION RESISTANCE

V. V. Tavgen',[1] S. P. Rodtsevich,[1] and T. S. Minkevich[1]

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The properties of alkali borotitanium-silicate glasses with different content of boron, titanium, and lithium oxides are investigated. It is indicated that glasses with a low content of B_2O_3 (8 – 10%) can be used to produce white glass-enamel coatings that have enhanced corrosion resistance and low leachability of the coating components in acetate solutions.

Glass-enamel coatings represent the most common and reliable way to protect steel products, including kitchen utensils, from corrosion. The requirements on the quality of enameled kitchenware are becoming higher, regarding both their exterior appearance and corrosion resistance. The requirements on corrosion resistance of glass-enamel coatings have sharply grown after the adoption of the new Sanitary Regulations on migration of chemical elements from materials contacting food items (SanPiN 13-3 RB 01). The stricter requirements on migration of boron, nickel, and cobalt from a coating to acetate extracts, as well as the introduction of regulations on leaching of aluminum, titanium, and iron make it necessary to produce enamels with higher chemicals resistance.

Silicate glasses for protective coatings are multicomponent, which makes it possible to vary their properties within wide ranges; however, the list of materials for the synthesis of white titanium enamels is limited. The compositions of white enamel have been refined over the past decades and a further improvement in their chemical resistance, while preserving other technological parameters, is hard to achieve. On the one hand, it is known [1 – 3] that to increase the chemical resistance of glasses it is primarily necessary to increase their content of silicon and titanium oxides and to decrease their content of boron oxides and alkali metals oxides, which strengthens the silicon-oxygen skeleton and the glass structure, but, on the other hand, this has a negative effect on the technological and service properties of coatings.

The present paper describes the study of alkaline borotitanium-silicate glasses with a higher content of silicon oxide compared to industrial compositions (GOST 24405–80) and a lower content of B_2O_3. Considering the valuable and actually indispensable role of boron oxide in enamel compositions responsible for decreasing viscosity and surface tension of melts, lowering the softening and firing temperature of coating, and facilitating the crystallization of anatase, it becomes obvious that B_2O_3 cannot be completely eliminated from the composition. At the same time, the target of decreasing boron leachability from coatings motivates the search for compositions with a lower content of B_2O_3 and methods for stronger fixation of boron in the glass structure. The undesirable phenomena related to the decreased content of boron oxide were compensated by additional introduction of lithium oxide, which has a favorable effect on acid resistance of glasses and decreasing the glass melt viscosity.

We investigated the properties of four series of glasses that contain (%; here and elsewhere weight content): 6, 8, 10, and 12 B_2O_3 and, respectively, 24, 22, 20, and 18 TiO_2. At the same time, sodium oxide was partly replaced by lithium oxide. The total content of alkali oxides ($Li_2O + Na_2O + K_2O$) was 14.5% and the amount of other components (SiO_2, P_2O_5, MgO, Al_2O_3, and F) remained constant.

Experimental glasses were synthesized from chemically pure reactants and quartz sand OVS-015 from the Novoselovskoe deposit. The glasses were melted in porcelain crucibles in an electric furnace with Silit heaters at a temperature of 1350°C with an exposure of 30 min.

Under the specified conditions, the glasses were completely melted and had good working properties (except for the glass in the first series with 2% Li_2O). The glass containing 2% Li_2O, 6% B_2O_3, and 24% TiO_2 had insignificant opalescence.

[1] Institute of General and Inorganic Chemistry of the National Academy of Sciences of Belarus, Minsk, Belarus.

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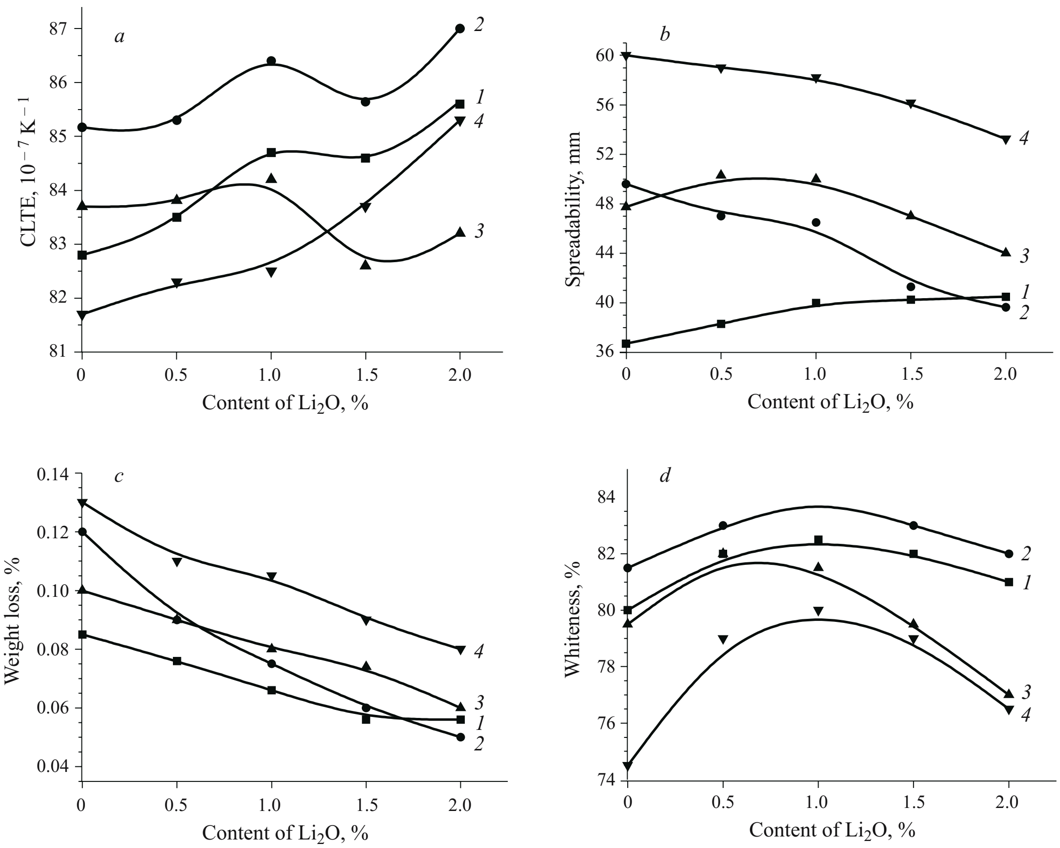

Fig. 1. Variations in CLTE (*a*), spreadability at 860°C (*b*), and chemical resistance (*c*) of glasses and whiteness of coatings (*d*) depending on Li_2O content: *1*) 6% B_2O_3 and 24% TiO_2; *2*) 8% B_2O_3 and 22% TiO_2; *3*) 10% B_2O_3 and 20% TiO_2; *4*) 12% B_2O_3 and 18% TiO_2.

The CLTE of the considered glasses is within the limits of $(81 - 87) \times 10^{-7}$ K^{-1} and has a general tendency to increase as sodium oxide is replaced by lithium oxide, which may be due to the increasing total molar content of alkali oxides.

The effect of boron oxide content is more complicated: as the B_2O_3 content grows from 6 to 8%, the CLTE of glass grows, whereas with a higher B_2O_3 content (10 – 12%) it decreases (Fig. 1*a*). The softening temperature of glasses is 535 – 575°C and decreases as the content of lithium and boron oxides increases.

The spreadability of glasses is the most important technological parameter, which to a great extent depends on boron oxide content and regularly decreases, when the content of boron oxide decreases (Fig. 1*b*). A certain decrease in the spreadability when sodium oxide is replaced by lithium oxide is related to the enhanced crystallization capacity of lithium-bearing glasses.

The chemical resistance of glasses is a very important parameter in estimating the service properties of glasses. The resistance of glasses to 4% solution of acetic acid regularly decreases with boron oxide content increasing from 6 to 12% (Fig. 1*c*). Replacing sodium oxide by lithium oxide raises acid resistance in all glasses, i.e., decreases weight losses under acid treatment. It should be noted that all glasses have low losses when boiled in acetic acid (less than 0.14%), which gives reason to expect high chemical resistance in coatings based on some lithium-free glasses.

All glasses considered at the firing temperature of 820°C produce coatings on steel, whose exterior appearance and quality differs substantially depending on their composition. As the content of boron oxide grows, the firing interval of coating is shifted toward lower temperatures. The replacement of sodium oxide by lithium oxide and raising boron oxide content in titanium glasses from 6 to 8% improve the quality of the coating surface and the whiteness parameter grows to 84% with 1.0% Li_2O (Fig. 1*d*, curve *2*). A further increase in B_2O_3 content to 10 and 12% decreases the whiteness of coatings (Fig. 1*d*, curves *3* and *4*).

In all glasses with lithium oxide content over 1.0%, the coatings acquire a yellowish-gray shade, which is related to the crystallization of various modifications of titanium oxide: anatase and rutile. The introduction of initial additives (0.5%) of lithium oxide instead of sodium oxide intensifies the lines of anatase (Fig. 2). The maximum quantity of anatase is registered by x-ray phase analysis in heat-treated glasses containing 0.5 and 1.0% Li_2O. Increasing the content of Li_2O to 1.5 – 2.0% results in the prevailing crystallization

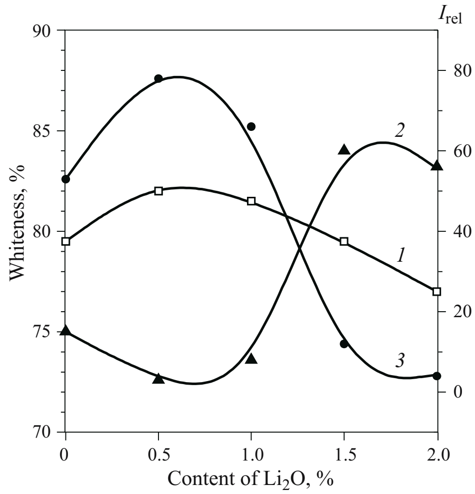

Fig. 2. Variation in the whiteness of coatings (*1*) and relative concentration of rutile (*2*) and anatase (*3*) in heat-treated glasses with different Li_2O content.

of rutile, and, accordingly, the whiteness of the coating decreases.

The glasses of the first series containing 6% B_2O_3 and 24% TiO_2, despite having high acid resistance, have an enhanced tendency for crystallization and poor spreadability at the firing temperature of the coating. The optimum properties are observed in glasses of the second and third series containing 8 – 10% B_2O_3 and 20 – 22% TiO_2, lithium-free or with small additives of Li_2O. The acid resistance of coatings based on such glasses (weight loss in 4% solution of acetic acid) amounts to 0.05 – 0.09 mg/cm^2, i.e., is significantly lower than the values specified in GOST 24788–2001.

According to the laboratory studies of experimental samples of enameled dishware, the migration of different chemical elements from coatings to acetate extracts is (mg/dm^3): 0.280 – 0.710 for boron, 0.150 – 0.230 for aluminum, 0.290 – 0.470 for titanium, and 0.024 – 0.034 for iron.

Thus, it is found that it is possible to synthesize white cover-coat enamels of increased acid resistance for steel kitchenware in the studied composition range.

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